Progress in the development of segmented thermoelectric unicouples at the Jet Propulsion Laboratory

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ABSTRACT

A new version of a segmented thermoelectric unicouple incorporating advanced thermoelectric materials with superior thermoelectric figures of merit has been recently proposed and is currently under development at the Jet Propulsion Laboratory (JPL). This advanced segmented thermoelectric unicouple includes a combination of state-of-the-art thermoelectric materials based on Bi_2Te_3 and novel materials developed at JPL. The segmented unicouple currently being developed is expected to operate between 300 and about 975K with a projected thermal to electrical efficiency of up to 15%. The segmentation can be adjusted to accommodate various hot-side temperatures depending on the specific application envisioned. Techniques and materials have been developed to bond the different thermoelectric segments together for the n- and p-legs and low contact. resistance bonds have been achieved. In order to experimentally determine the thermal to electrical efficiency of the unicouple, metallic interconnects must be developed for the hot side of the thermocouple to connect the n- and p-legs electrically. The latest results in the development of these interconnects are described in this paper. In addition, efforts are also focusing on the fabrication of a unicouple designed for thermal and electrical testing.

INTRODUCTION

The segmented unicouple under development incorporates a combination of state-of-the-art thermoelectric materials and novel p-type Zn_4Sb_3, p-type $CeFe_4Sb_{12}$-based alloys and n-type $CoSb_3$-based alloys developed at JPL. In a segmented unicouple as depicted in Figure 1, each section has the same current and heat flow as the other segments in the same leg. Thus in order to maintain the desired temperature profile (i.e. keeping the interface temperatures at their desired level) the geometry of the legs must be optimized. Specifically, the relative lengths of each segment in a leg must be adjusted, primarily due to differences in thermal conductivity, to achieve the desired temperature gradient across each material. The ratio of the cross sectional area between the n-type and p-type legs must also be optimized to account for any difference in electrical and thermal conductivity of the two legs. A semi-analytical approach that includes smaller effects such as the Peltier and Thompson contributions and contact resistance in order to optimize and calculate the expected properties of the device has been used to solve the problem [1]. For each segment, the thermoelectric properties are averaged for the temperature range it is used. At each junction (cold, hot, or interface between two segments), the relative lengths of the segments are adjusted to ensure heat energy balance at the interface. Without any contact resistance between segments, the efficiency is not affected by the overall length of the device; only the relative length of each segment needs to be optimized. The total resistance and power output, however, does depend on the overall length and cross sectional area of the device. The calculated optimized thermoelectric efficiency is about 15% with the hot junction at 975K and the cold junction near room temperature. The optimal geometry is illustrated in Figure 1.

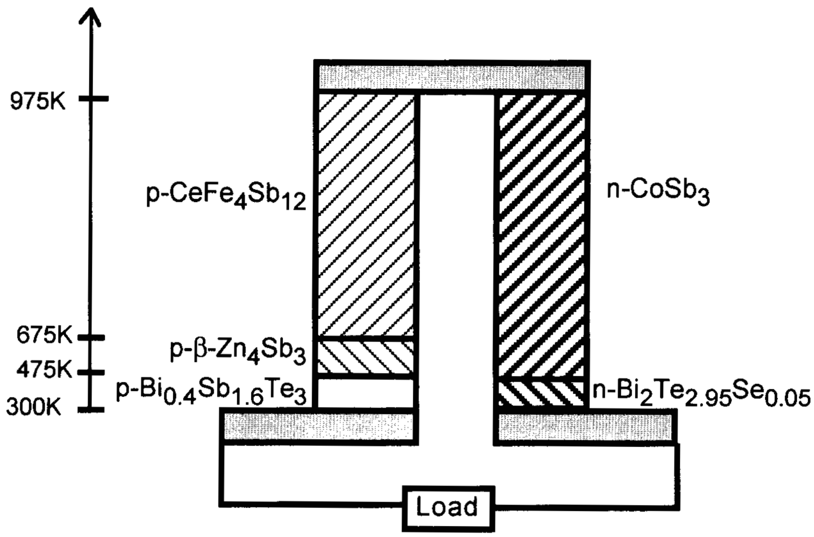


Figure 1. Illustration of the advanced unicouple incorporating new high performance thermoelectric materials. The relative lengths of each segment and the cross-sectional areas for the p- and n-legs are drawn to scale. The calculated thermoelectric efficiency is about 15%.

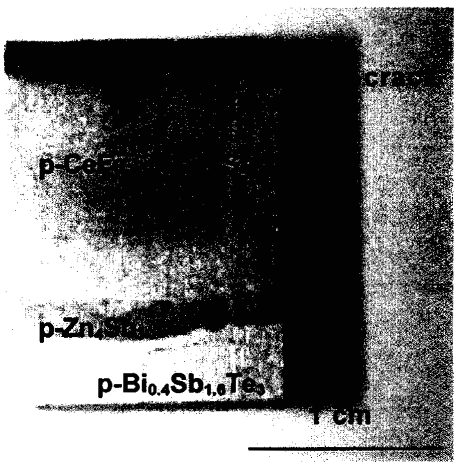
High contact resistance between the thermoelectric segments and the thermoelectric segments and interconnects at the cold and hot-sides can dramatically reduce the efficiency of a generator. Calculations show that a low contact resistance, less than about 20 $\mu\Omega cm^2$, is required to keep the efficiency from being significantly degraded by the contact resistance. Techniques and materials have been developed to bond the different thermoelectric segments of the unicouple together [2]. Electrical contact resistance lower than 5 $\mu\Omega cm^2$ have been obtained for each of the junctions at its projected operating temperature. The n- and p-legs have also been successfully connected to a "cold shoe" for heat transfer to the heat sink using a Bi-Sn solder and Ni as a diffusion barrier [2]. While some success has been achieved in brazing Nb metal to the top skutterudite segments [2] using a $Cu_{28}Ag_{72}$ alloy, the relatively high brazing temperature required (780°C) may impact the mechanical integrity of the legs after brazing. Some alternative ways of creating metallic interconnects for the hot-side of the legs have been explored and the results are reported in this paper.

EXPERIMENTAL PROCEDURES

Since both entire n- and p-segmented legs can be fabricated by uniaxial hot-pressing the various thermoelectric materials separated by thin metallic foils [2], an alternative approach to create a metallic layer on the top of the legs is to add some metallic powder on the top of the legs during the hot-pressing. Two type of metals were investigated : Ni and Nb. In some cases entire legs were fabricated with the top metallic portion while in some other cases only the top skutterudite materials were hot-pressed with the metallic powders. After pressing, a small strip of the samples was polished along the pressing axis to reveal the microstructure of the junction which was investigated by both optical microscopy and electron microprobe analysis. In addition, the electrical contact resistance was measured by a four probe technique up to the predicted optimum temperature of operation. One voltage probe is located at one end of the sample while the second probe can move along the sample. The variations of the electrical contact resistance is therefore recorded as a function of the distance of the moving probe to the fixed probe.

RESULTS AND DISCUSSION

Figures 2 and 3 show samples of cut p- and n-entire, hot-pressed legs with Ni as the top metallic segment. The density of the hot-pressed Ni was determined to be 91% of the theoretical density. Microprobe analysis of the Ni/skutterudites interface showed a good quality bond. However, in both cases, lateral cracks are visible within the skutterudite materials in the region adjacent to Ni. This is probably due to the relative large difference between the thermal expansion of Ni, 13.3 x 10^{-6}/K, compared to those for p-$CeFe_4Sb_{12}$ and n-$CoSb_3$, 7.5 and 6.36 x 10^{-6}/K, respectively.



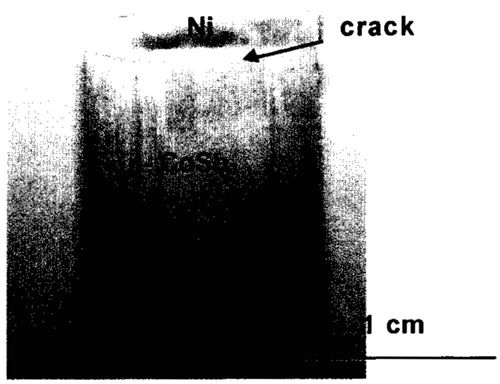


Figure 2. Photograph of a three segments p-leg cut in half and with Ni as the top metallic interconnect. Cracks are visible in the top thermoelectric material next to the interface with Ni.

Figure 3. Photograph of a two segments n-leg cut in half and with Ni as the top metallic interconnect. Cracks are visible in the top thermoelectric material next to the interface with Ni.

Figures 4 and 5 show for p-$CeFe_4Sb_{12}$/Nb and n-$CoSb_3$/Nb junctions after hot-pressing. Microprobe analysis of the Nb/skutterudites interface regions showed a good quality bond. No cracks were observed in the skutterudite materials which is presumably due to the reasonable match between the thermal expansion coefficient of the skutterudite materials and that of Nb (7.1 x 10^{-6}/K)

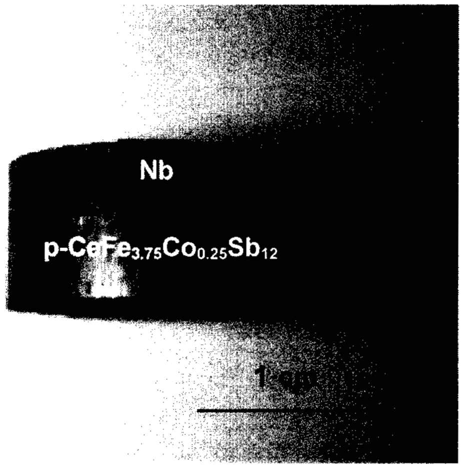


Figure 4. Photograph of a Nb/p-$CeFe_{3.75}Co_{0.25}Sb_{12}$ junction fabricated by hot-pressing. No cracks are visible in the skutterudite material.

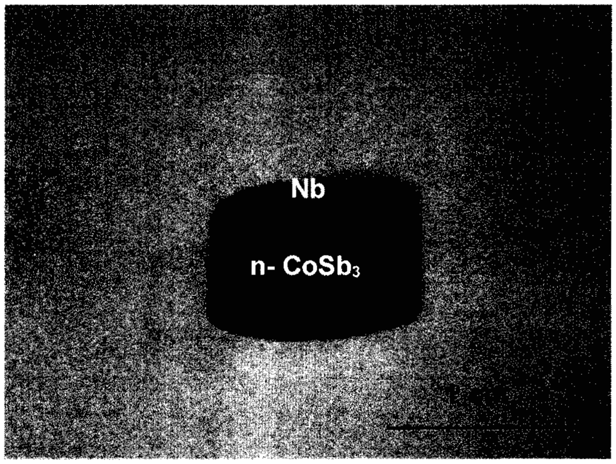


Figure 5. Photograph of a Nb/n-$CoSb_3$ junction fabricated by hot-pressing. No cracks are visible in the skutterudite material.

The electrical contact resistance between the skutterudite materials and hot-pressed Nb powder was measured and the results are reported in Figures 6 and 7. The results show that electrical resistance lower than 5 $\mu\Omega cm^2$ were achieved at temperatures close to the projected operation temperature. No Nb diffusion into the skutterudite materials was observed by microprobe analysis. The density of the hot-pressed Nb powder was determined to be about 80% of the theoretical value which results in an increased electrical resistivity and could potentially increase the total resistance of the unicouple. The added resistance due to the addition of 1.5 mm of hot-pressed Nb on the top of 1.5 cm long segmented legs would however result in a negligible 0.41% of the total resistance of the unicouple. Once both n- and p-legs can be fabricated with a Nb layer of hot-pressed Nb on the top they would have to be joined by an electrical connector. For electrical and thermal performance testing of the unicouple, this connector could also be used as a heater. A 12 mm diameter heater was fabricated out of Nb. It is composed of a heating element introduced into a Nb shell filled with an electrically insulated refractory cement. Brazing of Nb metallic samples to hot-pressed Nb samples was successfully achieved at temperatures as low as 600°C using a $Cu_{22}Ag_{56.2}Zn_{17}Sn_5$ brazing alloy. The resulting bond was found to be of good mechanical quality and no electrical contact resistance was measured at the interface. Fabrication of an entire unicouple with Nb heater brazed on the top of the legs is currently underway.

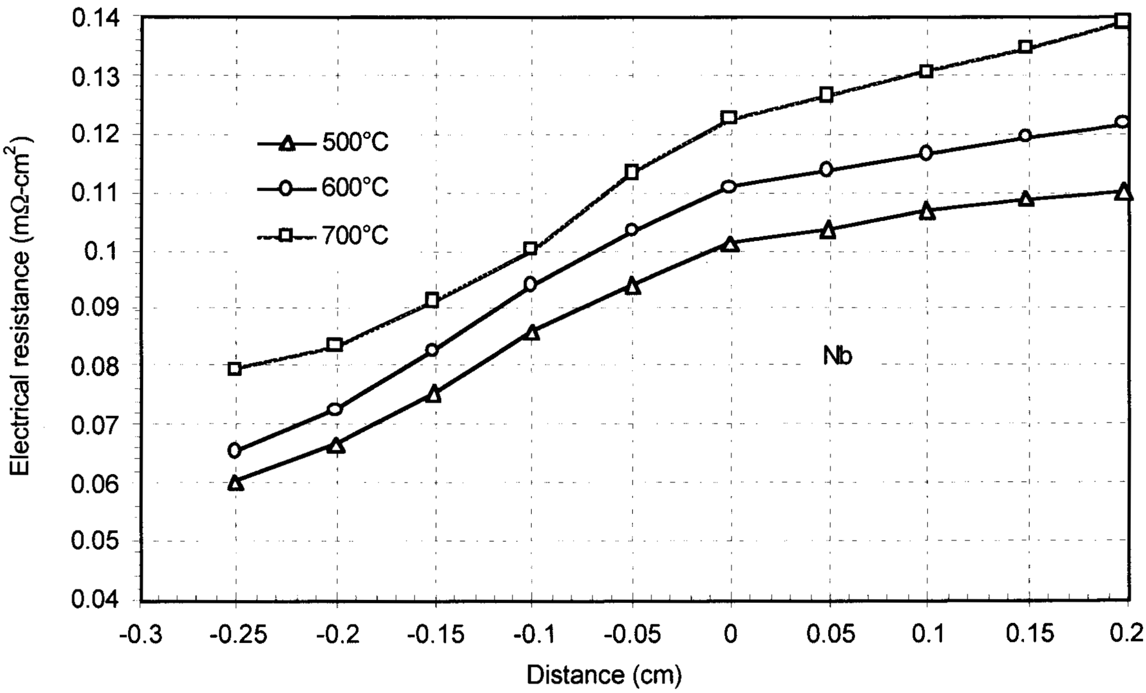


Figure 6. Electrical contact resistance as a function of distance for a hot-pressed n-$CoSb_3$/Nb junction. The origin corresponds to the interface position.

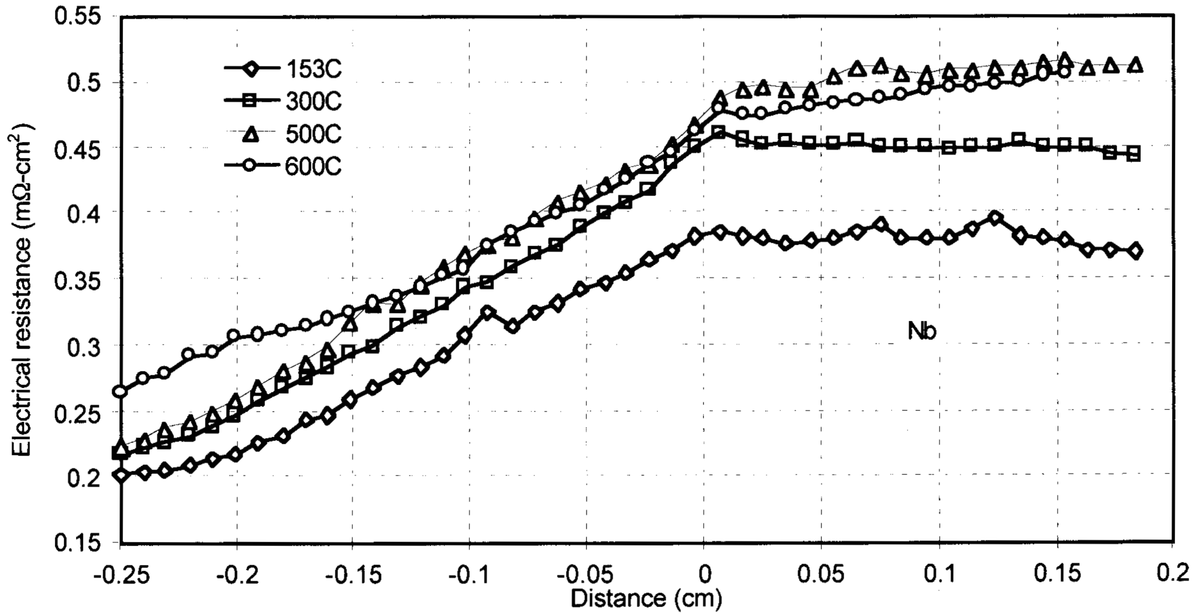


Figure 7. Electrical contact resistance as a function of distance for a hot-pressed p-$CeFe_4Sb_{12}$/Nb junction. The origin corresponds to the interface position.

CONCLUSION

Some alternative ways of creating metallic interconnects for the hot-side of segmented legs of an advanced thermoelectric unicouple have been explored. Hot-pressing Nb on the top of the segmented thermoelectric legs seem to provide a good electrical and mechanical bond. In addition, hot-pressed Nb was successfully brazed to a custom made Nb heater. The most critical technical issues associated with the fabrication of an advanced unicouple designed for thermal and electrical testing have been addressed. Efforts are currently focusing on the fabrication of a unicouple to experimentally determine its efficiency.

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